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Key Points:

- pCO$_2$ remained rather constant in boreal inland waters over the past two decades
- Long-term trends in DOC concentration and pCO$_2$ in inland waters are uncoupled
- Changes in runoff patterns most likely explain the observed uncoupling between DOC and pCO$_2$

Supporting Information:

- Supporting Information S1
- Table S1

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No long-term trends in pCO$_2$ despite increasing organic carbon concentrations in boreal lakes, streams, and rivers

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Abstract Concentrations of dissolved organic carbon (DOC) from terrestrial sources have been increasing in freshwaters across large parts of the boreal region. According to results from large-scale field and detailed laboratory studies, such a DOC increase could potentially stimulate carbon dioxide (CO_2) production, subsequently increasing the partial pressure of CO_2 (pCO$_2$) in freshwaters. However, the response of pCO$_2$ to the presently observed long-term increase in DOC in freshwaters is still unknown. Here we tested whether the commonly found spatial DOC-pCO$_2$ relationship is also valid on a temporal scale. Analyzing time series of water chemical data from 71 lakes, 30 streams, and 4 river mouths distributed across all of Sweden over a 17 year period, we observed significant DOC concentration increases in 39 lakes, 15 streams, and 4 river mouths. Significant pCO$_2$ increases were, however, only observed in six of these 58 waters, indicating that long-term DOC increases in Swedish waters are disconnected from temporal pCO$_2$ trends. We suggest that the uncoupling of trends in DOC concentration and pCO$_2$ are a result of increased surface water runoff. When surface water runoff increases, there is likely less CO_2 relative to DOC imported from soils into waters due to a changed balance between surface and groundwater flow. Additionally, increased surface water runoff causes faster water flushing through the landscape giving less time for in situ CO_2 production in freshwaters. We conclude that pCO$_2$ is presently not following DOC concentration trends, which has important implications for modeling future CO_2 emissions from boreal waters.

1. Introduction

Over the last two decades increasing dissolved organic carbon (DOC) concentrations, mostly derived from the terrestrial environment, have been observed in surface waters across the Northern Hemisphere and especially in the boreal region [*Evans et al.*, 2005; *Filella and Rodriguez-Murillo*, 2014; *Monteith et al.*, 2007]. Some argue that DOC trends are consistent with changes in temperature and hydrology [*Eimers et al.*, 2008; *Worrall and Burt*, 2007], while others propose that increasing DOC trends result from a reduction of anthropogenic sulfur in the atmosphere with a subsequent decrease in acid deposition [*Evans et al.*, 2006; *Monteith et al.*, 2007; *Roulet and Moore*, 2006; *Vuorenmaa et al.*, 2006]. The key drivers behind increasing DOC concentrations in Swedish surface waters during the past decades have been suggested to be changes in runoff combined with a decline in sulfate (SO_4^{2-}) deposition [*Erlandsson et al.*, 2008].

Consequences of increasing DOC concentrations can be many, ranging from enhanced metal concentrations to decreased water transparency and changes in pH and alkalinity [*Effler et al.*, 2010; *Kopacek et al.*, 2003; *Lead et al.*, 1999]. Even elevated surface water partial pressure of carbon dioxide (pCO$_2$) has been related to higher levels of DOC concentrations across temperate and boreal lakes [*Lapierre and del Giorgio*, 2012; *Sobek et al.*, 2005, 2003]. Biological and photochemical degradation of DOC has been suggested as an important factor underlying this positive relationship between DOC and carbon dioxide (CO_2) concentrations [*Graneli et al.*, 1996; *Lapierre et al.*, 2013]. Photochemical oxidation can directly transform allochthonous DOC to CO_2 as well as produce lower molecular weight fractions of DOC available for bacterial mineralization [*Tranvik and Bertilsson*, 2001]. Allochthonous DOC may also be directly degraded by biological processes and subsequently converted to CO_2 in freshwaters [*Guillemette et al.*, 2013; *McCallister and del Giorgio*, 2012]. Increases in DOC concentrations usually have an immediate effect on lake internal CO_2 production according to incubation experiments. For boreal lake waters it has, for example, been observed that each 1 mg L^{-1} DOC concentration increase results in a lake internal CO_2 production flux increase by about 28 mg C m^{-2} d^{-1} [*Algesten et al.*, 2005].

Lake internal biological mineralization of DOC has traditionally been suggested to account for most of the widespread CO_2 supersaturation of lakes [*Cole et al*., 2000; *del Giorgio and Peters*, 1994; *Jonsson et al*., 2001]. However, over the past years a number of studies have suggested that the observed CO_2 supersaturation could not be explained merely by net heterotrophy but that an additional, sometimes even dominant, fraction of external CO_2 input from the catchment via surface, subsurface, and groundwater flow is necessary to retain the high in-lake CO_2 concentrations [*Maberly et al*., 2013; *McDonald et al*., 2013; *Stets et al*., 2009; *Weyhenmeyer et al*., 2015b]. Whether the CO_2 is produced in the catchment and delivered via inflowing waters or produced within the water column through in situ carbon transformation processes could potentially be distinguished through the use of carbon stable isotopes ($\delta^{13}C$) of dissolved inorganic carbon (DIC) [*Aravena et al*., 1992; *Atekwana and Krishnamurthy*, 1998], but these data are not avaliable on larger scales. However, despite debates on the sources of CO_2 in waters, there is more agreement on the sources of DOC. In boreal lakes, usually more than 90% of the mineralized DOC is of allochthonous origin [*Jonsson et al*., 2001].

Although a positive relationship between DOC and surface water pCO_2 has frequently been reported [*Lapierre and del Giorgio*, 2012; *Sobek et al*., 2005, 2003], the effect of a long-term DOC increase on pCO_2 in freshwaters is still unknown. There are two possible scenarios that both would result in a concurrent DOC and pCO_2 increase: CO_2 is produced through mineralization of allochthonous DOC, with higher production rates at higher DOC concentrations, or CO_2 concentrations simply covary with DOC concentrations; i.e., both DOC and CO_2 originate from the same terrestrial source without further major transformation. The second scenario has recently been described by *Seekell and Gudasz* [2016]. They suggested that DOC and pCO_2 can covary due to recovery from acidification. Both DOC and pCO_2 are highly sensitive to acidification-induced changes in ionic strength of soils [*Evans et al*., 2005; *Lozanovska et al*., 2016]. In Sweden, recovery from acidification is also apparent, seen by decreasing SO_4^{2-} concentrations in waters [*Weyhenmeyer*, 2008] and increasing alkalinity [*Futter et al*., 2014]. However, during the past years recovery from acidification has leveled out and instead climate change effects, in particular precipitation and runoff changes, seem to drive DOC concentration increases [*Weyhenmeyer et al*., 2014].

Irrespective of whether DOC and pCO_2 covary or if CO_2 is mainly produced within the water column through mineralization of DOC, we expect pCO_2 to increase when DOC concentrations increase. We therefore hypothesize that Swedish freshwaters with a significant DOC increase over time also show a significant pCO_2 increase. We further hypothesize that DOC to pCO_2 relations are different between lakes, streams, and river mouths. In lakes we expect that in situ mineralization of DOC is the more important process driving CO_2 production, this becoming more apparent in lakes with longer water residence time since in these waters there is generally more time available to efficiently mineralize DOC to CO_2 [*Algesten et al*., 2004]. In streams and river mouths water flows faster; hence, there is less time for in situ carbon transformation processes. Consequently, in streams and river mouths we expect that trends in DOC and pCO_2 are mainly driven by catchment processes; i.e., they strongly covary.

2. Materials and Methods

2.1. Lake, Stream, and River Mouth Data

In this study we used water chemical data from 178 lakes, 86 streams, and 42 river mouths distributed across all of Sweden, covering both the boreal and hemiboreal regions (Figure 1). The water chemistry data were acquired from the Swedish national freshwater monitoring program [*Folster et al*., 2014]. Data acquired were: total organic carbon (TOC), conductivity, pH, alkalinity, total phosphorous (total P), and SO_4^{2-}. All water samples were collected at 0.5 m depths, except in more shallow streams where samples were taken closer to the surface. Many surface waters in Sweden have been limed since the late 1970s to counter surface water acidification caused by acid deposition [*Henrikson et al*., 1995]; however, none of the limed waters were included in this study.

All chemical analyses were performed at the SWEDAC (Swedish Board for Accreditation and Conformity) accredited laboratory at the Swedish University of Agricultural Sciences following standard limnological procedures. Analytical methods used can be found at http://www.slu.se/en/departments/aquatic-sciences-assessment/laboratories/geochemical-laboratory/water-chemical-analyses/. The data are made freely

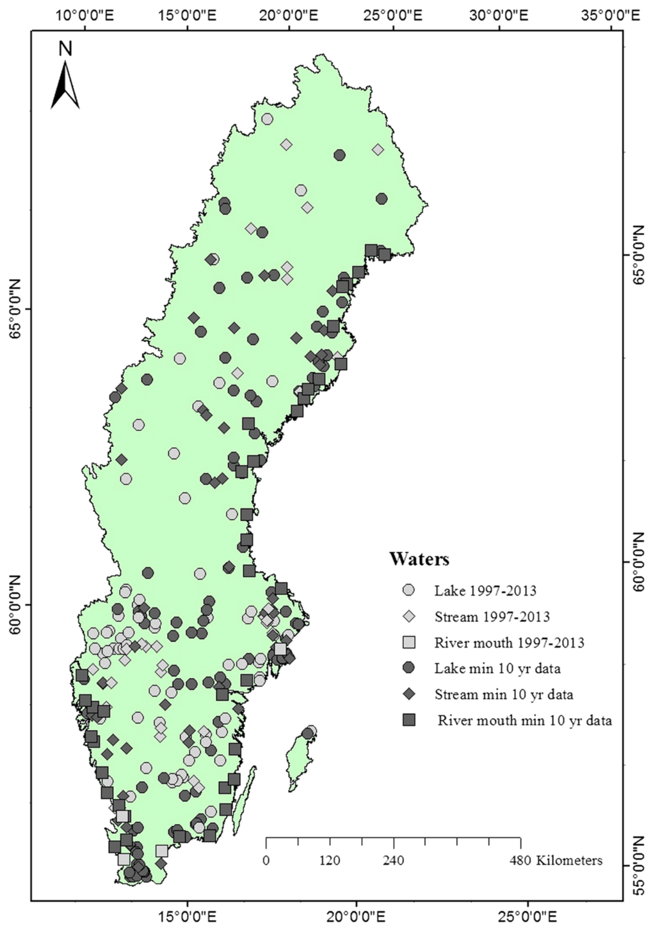

Figure 1. Location of the Swedish study lakes (circles), streams (diamonds), and river mouths (squares). Grey symbols show waters with complete time series during 1997–2013; black symbols show waters with shorter time series but which have at least 10 years of data.

available by the Swedish University of Agricultural Sciences and can be downloaded from http://www.slu.se/vatten-miljo. Total organic carbon concentrations were used as a proxy for DOC concentrations as the particulate fraction of organic carbon in boreal and hemiboreal freshwaters generally is less than 1% [*Laudon et al*., 2011]. All analyses considered in this study were made on unfiltered water.

From the collected data, concentrations of CO_2 were calculated using water temperature, alkalinity (only positive values were selected), and pH (only values >5.4 were used to minimize incorrect estimates of CO_2 concentrations; see below) according to *Weyhenmeyer et al.* [2012]. Subsequently, pCO_2 (in microatmospheres) were determined based on calculated CO_2 concentrations and Henry's constant according to Henry's law and adjusted for atmospheric pressure at sample site elevation [*Weyhenmeyer et al*., 2012]. Calculation of pCO_2 from alkalinity and pH may result in overestimated values, and CO_2 cannot be calculated from pH values of less than 5.2 [*Abril et al*., 2015; *Hunt et al*., 2011; *Raymond et al*., 2013]. Since also pH values slightly above 5.2 provide very uncertain estimates of pCO_2 [*Raymond et al*., 2013; *Wallin et al*., 2014], we minimized the uncertainty in the calculation of pCO_2 by discarding all pH values of less than 5.4. Calculations of pCO_2 are also uncertain in organic-rich waters. We removed the effect of organic acids on the total alkalinity by applying the triprotic model by *Hruska et al.* [2003] to estimate the dissociation of organic acid anions ($RCOO^-$) from measured pH and TOC. The calculated organic alkalinity was subtracted from the measured total alkalinity, and this new value for alkalinity was used to calculate pCO_2 according to *Weyhenmeyer et al.* [2012] followed by analyses for long-term trends in pCO_2. Finally, we minimized uncertainties in pCO_2 calculations by using median values rather than means to avoid the impact of outliers.

2.2. Data Analyses

For the data analyses we used two databases. Initial analyses were performed with the entire data set, i.e., waters for which there was a minimum of 10 years of data available (=database 1). The database comprised 178 lakes, 86 streams, and 42 river mouths distributed across all of Sweden (Figure 1). The lakes included in the analysis were mostly small, with a median surface area of 0.73 km^2, and shallow, having a median mean depth of 4.4 m. The lakes had been sampled between 10 and 28 years, while the longest sampling period for the streams was from 1959 to 2013, although some years were missing. Of the 86 streams, 11 had been sampled for 46 years. For the river mouths, samples had been collected for up to 27 years (Table 1).

As there was a wide range of sampling periods as well as some missing years of sampling for many waters, we used a subset of database 1 with complete data during 1997 to 2013 (= database 2). To make comparisons between sites, freshwaters with a minimum of four samples for each year were included. This resulted in a

Table 1. Number of Years Sampled, Longest Sampling Period, Years Missing in Longest Sampling Period, and Median Sampling Period for Lakes, Streams, and River Mouths Included in the Initial Analysis

	Number of Years Sampled	Longest Sampling Period	Years Missing in Longest Sampling Period	Median Sampling Period (Years)
Lakes	10 to 28	1983 to 2013	1985 to 1987	18
Streams	10 to 52	1959 to 2013	1961 to 1964	16
River mouths	10 to 27	1987 to 2013	-	13

total of 71 lakes, 30 streams, and 4 river mouths to be analyzed for long-term trends in DOC and pCO_2 (Figure 1). The lakes included in the second analysis were distributed across all of Sweden; however, there were more lakes in the southern parts (Figure 1). Lakes included in the second analysis were generally small, having a median surface area of 0.99 km^2, and shallow, with a median mean depth of 4.8 m. About two thirds of the streams included in the second analysis were distributed in the southern parts of Sweden. The four river mouths included in the analysis were all located in southern Sweden (Figure 1).

2.3. Statistics

All analyses were performed on yearly median values. Prior to analysis, data were tested for normality using the Shapiro-Wilk *W* test. Due to the nonnormal distribution of pCO_2, we chose the nonparametric Mann-Kendall trend test as it does not require normally distributed data. A Mann-Kendall trend test shows if there is a monotonic upward or downward trend of the variable of interest over time. We used an Excel macro for the Mann-Kendall trend test (Microsoft Office 2015) and the software package JMP version 11.0.0 (SAS Institute Inc. 2013) for all other calculations and statistical analyses. For all tests we set the significance at an alpha level of 0.05. When we determined a significant trend, the results were referred to as increase or decrease, whereas when we did not find any significant change, the results were referred to as no change.

3. Results

3.1. Overall Trends in DOC and pCO_2 in Lakes, Streams, and River Mouths

Of the 178 lakes included in the initial analysis, which encompassed all waters with a minimum of 10 years of data, there was a significant DOC concentration increase in 101 (i.e., 57%) lakes, while in the remaining 77 lakes, DOC concentrations did not show a significant trend over time. Of the 101 lakes with increasing DOC concentrations, 22 (i.e., 22%) also increased significantly in pCO_2 (Mann-Kendall trend test results: $p < 0.05$).

The long-term DOC patterns in streams were similar to lakes, i.e., in 42% of the 86 streams DOC concentrations had increased significantly (Mann-Kendall test: $p < 0.05$). Eight out of the 36 streams with increasing DOC concentrations (i.e., 22%) also showed a significant increase in pCO_2 (Mann-Kendall test: $p < 0.05$).

River mouths showed similar long-term DOC patterns with a significant increase in DOC concentration in 17 (40%) of the 42 river mouths. However, there was no significant increase over time in pCO_2 in any of the river mouths (Mann-Kendall test results $p > 0.05$).

3.2. Trends in Lakes During 1997 to 2013

During the period 1997 to 2013, lake DOC concentrations ranged between 0.6 and 25.1 mg L^{-1} across all lakes, with the lowest and highest values both occurring in 2005. More than half (39 out of 71) of the lakes demonstrated a significant increase in DOC concentrations, and four of these also showed a significant increase in pCO_2 (Mann-Kendall test: $p < 0.05$) (Figures 2 and 3 and Table S1).

Among the variables which potentially can have a strong influence on pCO_2 in waters, i.e., alkalinity, pH, SO_4^{2-}, and primary production (here we used total P concentrations as a proxy according to *Wetzel* [1992]) we found significantly increasing trends over time in alkalinity, pH, and total P concentrations in 13, 8, and 6 lakes, respectively, of the 39 lakes with significantly increasing DOC concentrations (Figure 3 and Table S1). In the majority (97%) of lakes with increasing DOC concentrations, SO_4^{2-} concentrations had decreased significantly (Mann-Kendall test: $p < 0.05$).

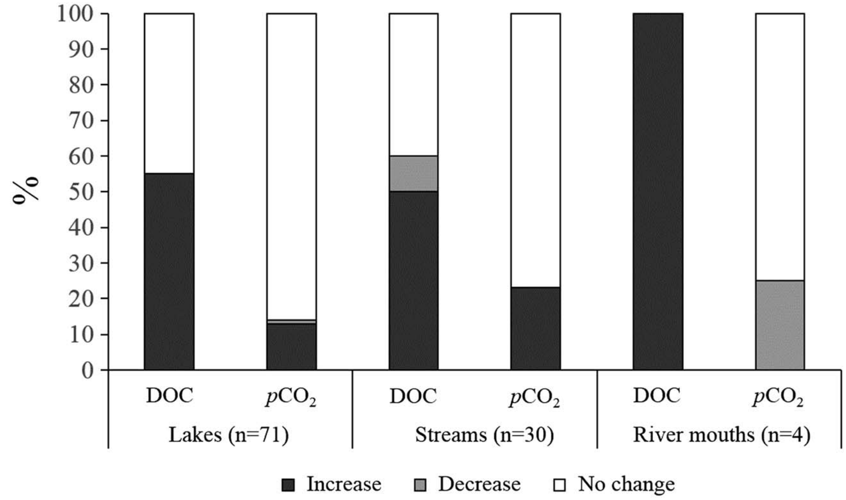

Figure 2. Percentage of surface waters of Swedish boreal lakes (n = 71), streams (n = 30), and river mouths (n = 4) with significant increase, decrease, or with no change in dissolved organic carbon (DOC) or partial pressure of carbon dioxide ($p CO_2$) during the period 1997 to 2013.

3.3. Trends in Streams During 1997 to 2013

In the study streams included in the second analysis, DOC concentrations ranged between 1.0 and 28.4 mg L^{-1} throughout 1997 to 2013. The highest stream DOC concentration occurred in 2009 and the lowest in 2013. Half of the streams (15 out of 30) showed a significant increase in DOC concentrations, and of these, only two demonstrated a significant increase in $p CO_2$ (Mann-Kendall test: $p < 0.05$; Figures 2 and 3 and Table S2).

Of the 15 streams with increasing DOC, alkalinity had increased significantly in five streams, pH in one stream, and total P in two streams (Figure 3 and Table S2). As seen in the lakes, most streams with increased DOC also showed a decrease in SO_4^{2-}, i.e., in 11 of the 15 streams.

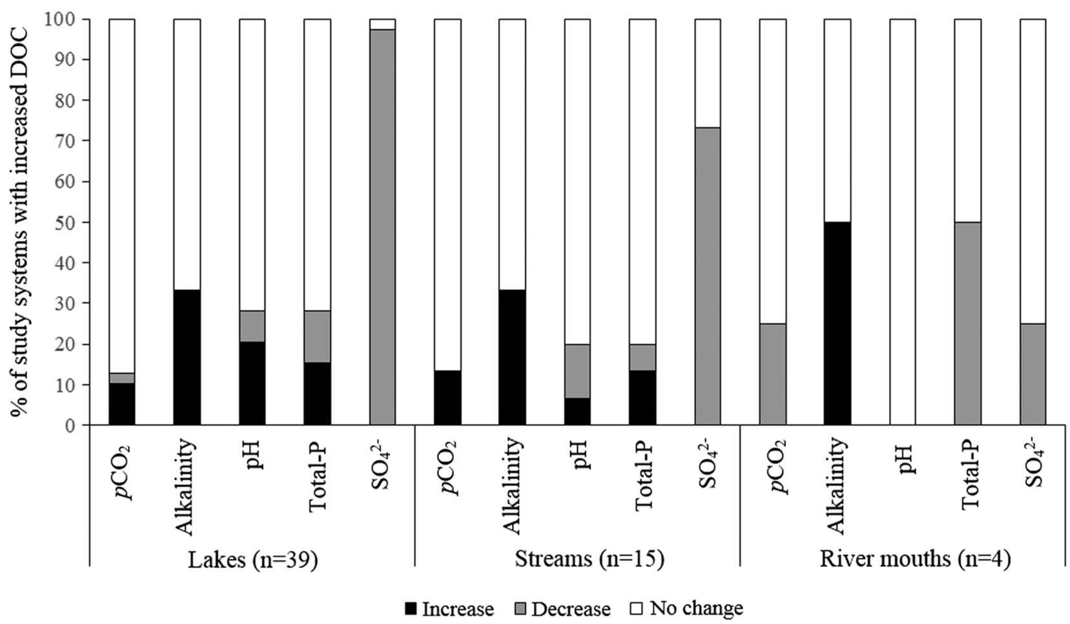

Figure 3. Percentage of Swedish boreal lake waters (n = 39), streams (n = 15), and river mouths (n = 4) with significant increase, decrease, or with no change in partial pressure of carbon dioxide ($p CO_2$), alkalinity, pH, total phosphorous (total P), and sulfate (SO_4^{2-}) concentrations during the period 1997 to 2013. All waters had increased significantly in dissolved organic carbon concentration (DOC) during this period.

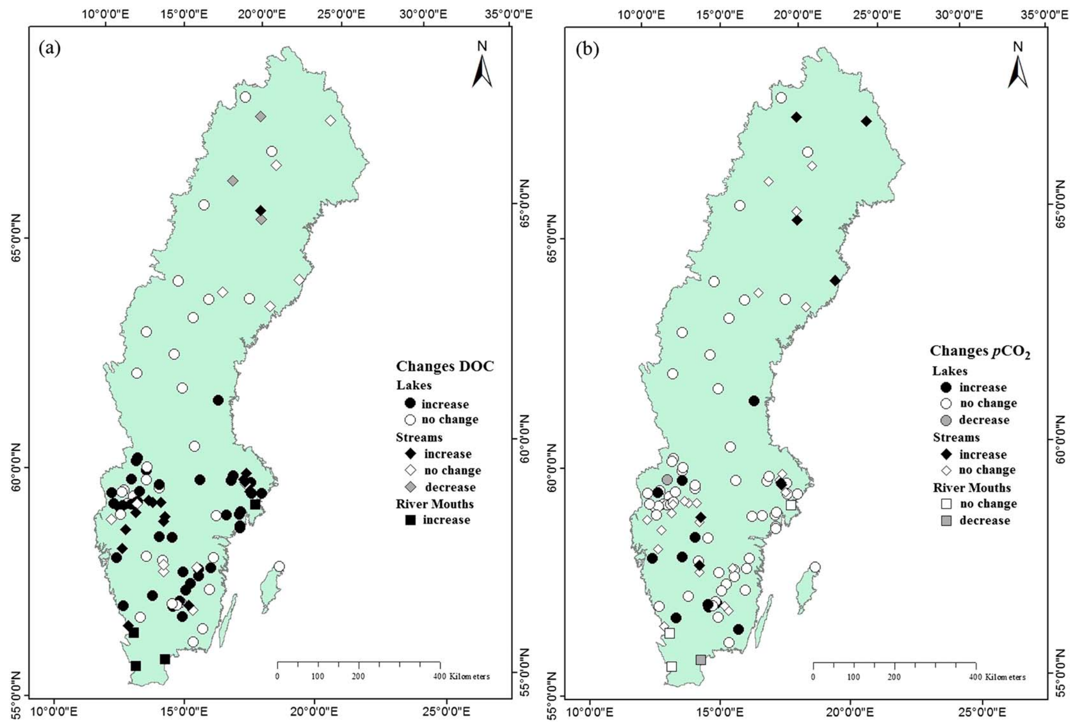

Figure 4. Location of Swedish study lakes (circles, $n = 71$), streams (diamonds, $n = 30$), and river mouth (squares, $n = 4$) and illustration of changes in (a) dissolved organic carbon (DOC) and (b) partial pressure of carbon dioxide ($p\mathrm{CO_2}$) in the surface waters (black = significant increase, white = no change, grey = significant decrease) during the period 1997 to 2013.

3.4. Trends in River Mouths During 1997 to 2013

During the period 1997 to 2013 river mouth DOC concentrations ranged from 6.9 to 22.7 mg $\mathrm{L^{-1}}$, with the lowest and highest measured concentrations occurring in 1998 and 2011, respectively. All four river mouths showed significant DOC concentration increases, but none showed a significant increase in $p\mathrm{CO_2}$ (Figure 2).

Alkalinity had increased in two of the four river mouths from 1997 to 2013, pH had increased in none, total P concentrations had decreased in two of the river mouths, and $\mathrm{SO_4}^{2-}$ had significantly decreased in one river mouth (Figure 3 and Table S3).

3.5. Spatial Variability in Trends Over Time

For all waters (lakes, streams, and river mouths) included in the second analysis, i.e., from 1997 to 2013, increases in DOC concentrations were mostly occurring in the southern parts of Sweden (Figure 4a). No obvious spatial pattern was observed for changes in $p\mathrm{CO_2}$ due to very few waters having significantly altered $p\mathrm{CO_2}$. However, most of the lakes with increased $p\mathrm{CO_2}$ were located in southern Sweden, whereas the streams with enhanced $p\mathrm{CO_2}$ were found both in the south and in the north of Sweden (Figure 4b).

4. Discussion

Our study clearly demonstrates that in the majority of Swedish freshwaters $p\mathrm{CO_2}$ has not changed significantly over the past decades despite significantly increasing DOC concentrations. These findings apply to lakes, streams, and river mouths. Thus, our hypothesis of concurrent DOC and $p\mathrm{CO_2}$ increases over time was supported in only six out of 58 freshwaters that had shown a significant increase in DOC concentrations. Consequently, trends over time in DOC and $p\mathrm{CO_2}$ are generally uncoupled across all types of Swedish freshwaters.

Originally, we had expected that increasing DOC concentrations go along with increasing $p\mathrm{CO_2}$ either due to increased lake internal $\mathrm{CO_2}$ production or due to increased lake external $\mathrm{CO_2}$ inflow together with the DOC

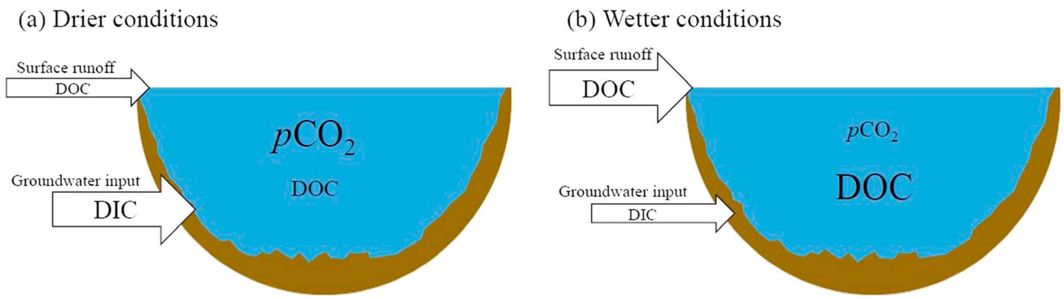

Figure 5. Conceptual model of the effect of hydrological processes on partial pressure of carbon dioxide (pCO_2) in freshwater. (a) During drier conditions freshwaters receive proportionally less shallow groundwater compared to dissolved inorganic carbon (DIC)-rich deep groundwater with subsequently higher pCO_2. (b) During more wet conditions shallower groundwater gets flushed into freshwaters diluting the DIC-rich deep groundwater such that an increase in dissolved organic carbon (DOC) does not result in increased pCO_2.

inflow. However, although we cannot rule out that more CO_2 is produced within the water column or that lake external CO_2 inputs through recovery from acidification or runoff increases have increased, there must be other overriding factors that result in relatively constant pCO_2 levels over time.

The lack of long-term trends in pCO_2 despite increasing DOC concentrations might be caused by an accelerated CO_2 loss from the water column. Such losses are, for example, possible when primary production increases. We found, however, decreasing rather than increasing total P concentrations (Figure 3), indicating that the CO_2 loss by primary production most likely has not substantially increased during the past years. In addition, primary production in the boreal waters has usually only a minor impact on the aquatic carbon cycling [*Algesten et al*., 2004], another reason why it is rather unlikely that CO_2 in the boreal waters has increasingly been lost over time due to increased primary production.

An alternative and more likely explanation to the lack of change in pCO_2 is a change in hydrology. Hydrological processes affect pCO_2 in freshwater in a number of ways. First, changes in runoff patterns alter the ratio between shallow and deep groundwater flow into lakes and streams [*Laudon et al*., 2007]. Streams typically have a strong hydrochemical connectivity with the catchment soils [*Hope et al*., 2004; *Laudon et al*., 2011]. Consequently, much of the CO_2 in streams comes from direct inputs of DIC, fixed and mineralized in the catchment and delivered via the groundwater [*Leith et al*., 2015; *Öquist et al*., 2009; *Winterdahl et al*., 2016]. A recent study demonstrated that in situ DOC mineralization was a minor source of CO_2 in small boreal headwater streams and that the main source of stream CO_2 was CO_2-rich groundwater [*Winterdahl et al*., 2016]. Likewise, *Weyhenmeyer et al.* [2015b] showed that direct inputs of DIC from the terrestrial surroundings of a lake have a stronger influence on CO_2 concentrations in lake water than do lake internal CO_2 production. As precipitation and runoff have shown an overall increase across Sweden over the past few decades, in particular during the 1990s and 2000s [*Bengtsson and Rana*, 2014; *Lindström and Bergström*, 2004; *Weyhenmeyer et al*., 2014, 2015a], we suggest that most waters now receive proportionally more shallow groundwater compared to deep groundwater [*Laudon et al*., 2007] (Figure 5). Such an increase most likely results in a DOC concentration increase in surface waters as DOC concentration in soil profiles tends to increase toward the top soil layers [*Grabs et al*., 2012; *Kaiser and Kalbitz*, 2012]. Although the literature is scarce, similar soil profiles of CO_2 concentrations do not show the same pattern due to soil CO_2 having a soil-atmospheric exchange resulting in higher CO_2 at deeper soil horizons [*Öquist et al*., 2009; *Winterdahl et al*., 2016]. Consequently, there would be a dilution effect on the DIC input from the terrestrial surroundings which could explain the lack of change in pCO_2 in response to enhanced DOC concentrations.

Hydrological processes also affect water retention time, both in the landscape and within water systems. The lake and stream internal CO_2 production shows a dependency on landscape water retention time with more efficient production in waters with a long water retention time [*Catalán et al*., 2016; *Hanson et al*., 2011]. Since precipitation and water flushing through the landscape, in particular through lakes, has generally increased across Sweden over the past decades [*Weyhenmeyer et al*., 2014, 2015a], we suggest that there could be less time available for mineralization of DOC in lakes, making DOC mineralization less efficient and resulting in a weaker direct coupling between DOC and pCO_2. Rather inefficient lake internal DOC mineralization in comparison to other processes might further be supported by our observations that DOC-pCO_2 long-term relationships were rather similar across lakes and streams.

All river mouths showed significantly increasing DOC concentrations, while none had an increase in pCO_2. We suggest that the DOC to CO_2 transformation in waters becomes less efficient during transport from headwaters down to the sea, as a response to faster water flushing through the landscape. Alternatively, the labile fractions of DOC are rapidly lost upstream, while the more recalcitrant DOC is transported downstream along the land to ocean continuum [*Creed et al*., 2015]. Consequently, when reaching the river mouth most of the DOC may consist of recalcitrant carbon which cannot be utilized by microbes.

The lack of change in pCO_2 despite increasing DOC concentrations could potentially also be a matter of DOC quality change as this affects the reactivity of DOC and thus its potential for mineralization to CO_2 [*Mostovaya et al*., 2016]. In general, DOC can be more humic or more protein-like [*Kothawala et al*., 2014]. Protein-like DOC is generally derived from autochthonous algae and microbes; it is often labile and biologically reactive and is both produced and degraded over time within aquatic systems [*Guillemette and del Giorgio*, 2011]. Humic-like DOC is generally derived from the terrestrial environment and is susceptible to within-lake processes and may be rapidly lost from the water column by mineralization, flocculation, or transformation to other DOC by-products [*Kothawala et al*., 2014]. Flocculation, in particular, is an important transformation process for humic-like DOC components as it has been shown that in lakes, up to 22% of terrestrially derived DOC can be lost from the water column merely from flocculation and subsequent sedimentation [*Einarsdottir et al*., 2017; *von Wachenfeldt and Tranvik*, 2008]. The observed increase in DOC in freshwaters in the present study is probably mostly of terrestrial origin, hence consisting of humic-like components [*Kothawala et al*., 2014]. Consequently, in the lakes, a significant amount of DOC may flocculate resulting in less carbon being available for CO_2 production. Flocculation may, however, not be as important in streams and river mouths as faster flowing water limit the period of time for flocculation and settling of organic matter [*von Wachenfeldt and Tranvik*, 2008]. Nonetheless, further studies are needed where the quality of the DOC is investigated to elucidate whether DOC quality plays an important role in pCO_2 changes through time.

Apart from biogeochemical processes, also uncertainties in our pCO_2 calculations might have caused some bias in the pCO_2 trends over time. Estimating pCO_2 from pH and alkalinity is commonly used in the literature [*Raymond et al*., 2013; *Sobek et al*., 2005; *Weyhenmeyer et al*., 2012] but has been criticized for being an uncertain method especially in acidic organic-rich waters with low alkalinity [*Abril et al*., 2015; *Hunt et al*., 2011; *Wallin et al*., 2014]. In the absence of long-term data sets of directly measured pCO_2, we, however, needed to rely on calculated pCO_2 in this study. Many of the waters in our study are organic-rich (median DOC = 8.8 mg L^{-1}) with low alkalinity (median alkalinity = 0.141 meq L^{-1}). We minimized uncertainties in the pCO_2 calculations by removing the effect of organic acids, excluding highly acidic waters, and performing all statistics on median values. Additionally, we used nonparametric methods where we considered relative rather than absolute pCO_2 values.

Still, pCO_2 trends over time might be affected by temporal changes in alkalinity and pH. Alkalinity has increased in more than half of the waters in our study during the period 1997 to 2013, whereas pH has generally remained constant. Alkalinity is a measure of the capacity of an aqueous solution to neutralize acids; hence, increased alkalinity is an indication of recovery from acidification. Consequently, the increased alkalinity observed in our study systems could reflect that Swedish freshwater systems have become less acidified [*Skjelkvale et al*., 2001]. According to *Seekell and Gudasz* [2016], recovery from acidification should result in increased pCO_2 in our lake types and not in constant or decreased pCO_2 as observed in this study. Increased alkalinity also implies that inorganic carbon concentrations have increased; however, as we do not see an increase in pCO_2, much of this carbon may exist as carbonates and bicarbonates. *Stets et al*. [2017] highlighted the importance of carbonate buffering for understanding CO_2 dynamics in freshwaters as CO_2 concentrations can be buffered despite large changes in the DIC pool. However, this effect is greatest in waters with high alkalinity and high pH. The systems in the study by *Stets et al*. [2017] had a median alkalinity of 2.78 meq L^{-1} whereas the majority (89%) of waters in our study had an alkalinity of less than 1.0 meq L^{-1}. Furthermore, only six of the waters in our study with alkalinity over 1.0 meq L^{-1} had increased in DOC, and of these only one stream and one river mouth had increased in alkalinity. Consequently, changes in alkalinity could potentially explain the lack of change in pCO_2 in these two waters. However, in the remaining 56 waters this is likely not the case due to the low alkalinity. *Stets et al.* [2017] suggested that in low alkalinity waters (< 1.0 meq L^{-1}) the pool of ionized CO_2 is small. Therefore, although alkalinity increased in many of our study waters, alkalinity is still low in the majority of the waters; hence, an increased buffering capacity could generally not explain the lack of change in pCO_2. Thus, the overall pattern of uncoupled DOC and pCO_2 long-term trends seems robust.

5. Conclusion

Although a positive relationship between DOC and pCO_2 has often been observed on a spatial scale, we were unable to establish a positive relationship on a temporal scale. Our results show that DOC concentrations and pCO_2 trends in lakes, streams, and river mouths through time are uncoupled and that changes in surface water runoff may explain this uncoupling. However, other processes, such as changes in alkalinity or DOC quality, may also be important for the fate of pCO_2, at least in some of the waters. To disentangle the relative importance of all these processes, additional detailed site-specific research is needed. It is striking, however, that there were no overall long-term pCO_2 trends despite increasing DOC concentrations. Since DOC concentrations are often used to predict pCO_2 and thereby CO_2 emissions from inland waters [e.g., *Raymond et al.*, 2013; *Sobek et al.*, 2003], predictions of future CO_2 emissions from inland waters need to consider the findings of this study. Although precipitation is predicted to further increase in the boreal region as a response to climate change [*Chen et al.*, 2015; *Teutschbein et al.*, 2015], presumably resulting in more DOC being flushed into inland waters, it is unlikely that pCO_2 will follow this increase.

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